Depth profile analysis of the valence state of Mn in a cycled lithium ion battery electrode

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INTRODUCTION

Lithiummanganate ($LiMn_2O_4$) was studied with X-ray L-edge emission spectroscopy. The manganate was present in the form of an electrode, which was electrochemically charged to 4.05 Volt and thereafter sliced for depth profile analysis. With this study we found that it is feasible to monitor oxidation state thickness profiles of electrodes and thus information about the spatial chemical homogeneity of the electrodes prior to and after cycling.

EXPERIMENTAL

$LiMn_2O_4$ was prepared from a stoichiometric mixture of Li_2CO_3 (J.T. Baker) and MnO_2 (Japan Metals, CMD). Details of electrode fabrication and cycling conditions are described in [1]. After charging, the electrode was removed from the cell and rinsed with Acetonitrile, and then dried. A scotch tape then was used to remove one thin layer of electrode material. This technique allows to reproducibly slicing a 50 micron thick electrode into about 10 to 20 parts. We have sliced the sample under consideration in 10 parts. Using a high precision laboratory balance it was possible to assign either slice the relative depth position in the electrode, with an accuracy of about 10%. 5 of these slices were subjected to manganese L-alpha emission spectroscopy at beamline 8 at the ALS with an excitation photon energy of 680 eV. Every sample was measured 4 times with an exposure time of 900 seconds each. The spectra for each sample were averaged and normalized.

RESULTS

Figure 1 shows the L-alpha and L-beta spectra of the manganese in the 5 samples. Minor, but systematic changes are observed in the range between 635 eV and 650 eV. The inset in Figure 1 shows a magnification of the spectra in this energy range. The spectra are shifted by each other, which is particularly visible between 640 eV and 645 eV. To quantify this effect, the first moment <E> of the intensity distribution was determined between 635 eV and 650 eV. A shift of the L-alpha spectra towards lower energy is indicative for a reduction of the manganese.

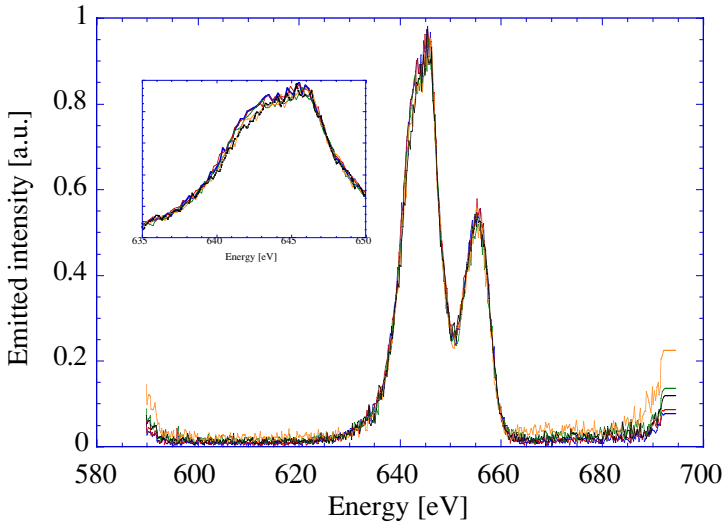

Figure 1: L-edge emission spectra obtained from 5 sample slices of one electrode. The inset shows a magnification of the spectra in the energy range from 635 eV to 650 eV, which is also the integration interval for <E>.

DISCUSSION

The manganese in $LiMn_2O_4$ spinel is present in two oxidation states: Mn3+ and Mn4+. Upon charging of the battery cell, major part of the lithium (about 90%) is electrochemically removed from the spinel lattice, with the result that the Mn3+ is oxidized to Mn4+. This reaction should take place more pronounced at the current collector site of the electrode, because conductivity is increased there. In contrast, at the separator site this reaction should take place slowlier. One therefore expects that – after charging - at the current collector there should be a higher concentration of Mn4+ than at the separator site. This expectation is confirmed by the experiment, as schematically displayed in Figure 2. The Sketch shows the lateral cross section of one battery half cell, in particular the aluminium current collector on the left, which meets the spinel electrode at the position x = 0. In the center, the spinel electrodes extends fro x = 0 to x = 50 µm, which is the sample top and meets the separator. Samples taken from the current collector site of the electrode assembly have spectra which are shifted towards lower energies, and they have a smaller first moment <E> than the spectra from samples which are further away from the current collector. For better view, the abscisse represents not the first moment <E>, but the difference 643-<E>, in eV.

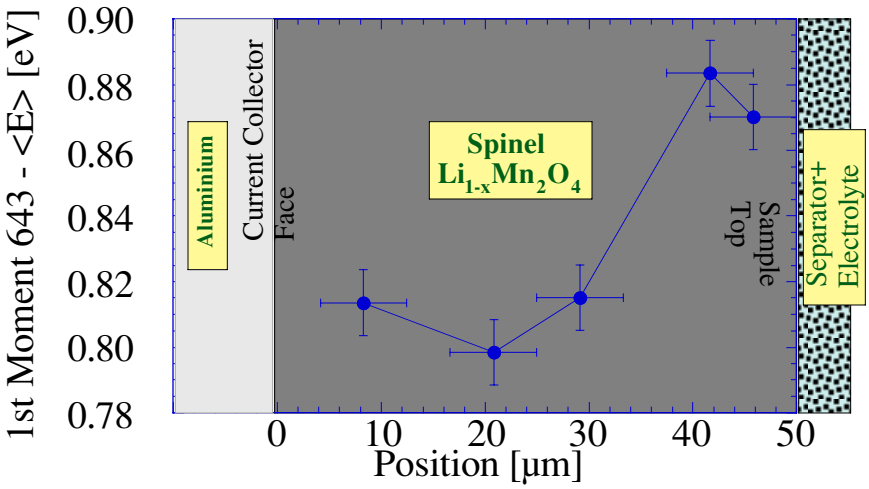

Figure 2: Schematic of a battery half cell, with inscribed first moment of the L-alpha emission peak versus the sample position.

With this novel sample preparation technique we are able to go beyond the regular spectroscopy experiments, which allowed only for spatial average oxidation states of samples. In future we will be able to monitor oxidation state variations in samples with a depth resolution of better than 5 microns. This will facilitate studies on the pathogenesis of battery electrodes during charging/discharging and possibly address engineering issues for the electrode design as well.

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